

REMARKS

This timely filed Reply is responsive to the Office Action dated June 2, 2004.

This Reply is accompanied by a Rule 132 Declaration from Dr. Harrison R. Cooper which is labeled as Exhibit "A".

Thirteen (13) claims were pending at the time of the Office Action. All claims were rejected. In this Reply, claims 8-10 and 13 have been amended and claims 14-17 have been added. No new matter has been added.

Claims 1-13 were determined to be obvious based on WO 98/54400 El Shall ("Shall '00") in view of U.S. Pat. No. 5,824,132 to Kopyleva et al. (Kopyleva). The U.S. version of "Shall '00" issued as U.S. Patent No. 6,632,327 to El-Shall. Dr. El-Shall is one of the current named inventors. Kopyleva is used by the Examiner for the proposition of generating phosphoric acid by acidulating a phosphate containing material. According to the Examiner:

El Shall disclose (see pages 3 and 9-11) a method of treating spent alkaline pulping liquor substantially as claimed. The claims differ from El Shall by reciting that the phosphoric acid is generated by acidulating a phosphate containing material. Kopyleva et al. disclose (see col. 1 line 15 through col 3 line 65) that it is known in the art to generate phosphoric acid by treating phosphate rock with sulfuric acid. It would have been obvious to one skilled in the art to modify the method of El Shall by utilizing the recited acidulating step in view of the teachings by Kopyleva et al., to aid in generating phosphoric acid for treating the black liquor. With regard to claim 13, it is submitted that the solid products produced from the use of the phosphoric acid of Kopyleva et al. in the method of El Shall are considered patentably indistinguishable from the solid products recited in the instant claims.

Applicants respectfully disagree with the Examiner's finding of obviousness for reasons described below. However, before reviewing the cited art, Applicants will first review the claimed invention recited in claim 1. Claim 1 recites a method of treating spent alkaline pulping liquor (black liquor), comprising the steps of providing black liquor having lignin therein, acidulating a phosphate containing material, wherein phosphoric acid is generated by treatment of the phosphate containing material, and mixing the black liquor with phosphoric acid from the acidulated phosphate containing material to cause separation of the lignin from the black liquor. Clarified liquor comprising anion species including phosphate, such as sodium phosphate are produced.

The products produced by Applicants' claimed process following causticizing with calcium oxide have been found to include substantial quantities of phosphatic material, including various forms of calcium phosphate. As described in the application (see particularly paragraph 29), this mixture can be an ideal soil amendment product due to slowly soluble phosphate, similar to single or triple super phosphates. Alternatively, the calcium phosphate can be in forms such as TCP which can be recycled to the acidulator. The value of the fertilizer products and/or phosphoric acid source produced following causticizing can be a significant factor in rendering Applicants' claimed process cost effective.

Added claims 14 and 15 recite that the phosphate containing material comprises low grade phosphate comprising rock, and the weight percentage of P_2O_5 in the low grade phosphate comprising rock is less than or equal to 29.5%, respectively. Applicants' Examples describe use low grade phosphate rock having a weight percentage of P_2O_5 of less than or equal to 29.5%.

The claimed method thus uses phosphoric acid as the strong acid derived from acidulating phosphate containing material, such as phosphate rock, instead of the sulfuric acid generally taught in El-Shall '00. Thus, causticizing with lime becomes successful as calcium phosphate is less soluble than calcium oxide. In contrast, using conventional sulfuric acid treatment for spent liquor, calcium sulfate is formed which has higher solubility than calcium oxide. Thus, calcium sulfate does not precipitate when the alkali sulfate solution is treated with burnt lime.

El-Shall '00 is entitled " Process for treating spent, waste, alkaline digestion liquor from paper pulping operations and product' discloses a water soluble, surface active, polymeric agent is mixed with digestion liquor, preferably with an additional surface active defoamer coagulant agent prior to or during acidification of the alkaline digestive liquor. The disclosed result is an easily separable, non-gelatinous, non-gummy, coagulated lignin as a solids, particulate fraction that tends to float on a clarified liquid fraction containing recoverable salts. The solids fraction and the liquid fractions are easily separated, one from the other, by a gravity separation step.

Although El-Shall '00 discloses that "conditioned liquor is passed to another station for its acidification with an acid, preferably sulfuric acid or phosphoric acid", all examples and other disclosure use of sulfuric acid for the acidification step. Moreover, as correctly noted by the Examiner, El-Shall '00 does not disclose obtaining phosphoric acid through the acidulation of phosphate containing material, such as phosphate rock.

Kopyleva is entitled "Method of phosphoric acid concentration" and discloses wet process phosphoric acid evaporation, its clarifying, fertilizer production and fertilizer

efficiency in the presence of multi-component mixture of anionic surfactants and ammonium compound. As noted in Kopyleva's Brief Description of Related Art:

The oldest economical process for making phosphoric acid is to treat phosphate rocks with sulfuric acid or with mixtures of sulfuric and phosphoric acid, precipitating calcium sulfate and releasing phosphoric acid. The last is called wet-process phosphoric acid. Generally it is desirable to concentrate this wet-process phosphoric acid and purify it. Purification may comprise the removal of coloring materials such as iron and vanadium after one or more stages of concentration. The wet-process phosphoric acid production is described fully in the Kirk Othmer Encyclopedia of Chemical Technology, (Second Edition) volume 9, p. 87.

Kopyleva does not disclose or suggest acidulating phosphate containing material (e.g. phosphate rock) for treatment of spent alkaline pulping liquor.

Applicants' claimed phosphoric acid-based method derived from phosphate containing material (e.g. phosphate rock) for treating spent alkaline pulping liquor has not been disclosed before, and moreover is non-obvious for several reasons. Applicants first note that sulfuric acid is used in commercial spent alkaline pulping liquor treatment because of the high cost of phosphoric acid as compared to sulfuric acid. Regarding phosphoric acid use, even if calcium phosphate is precipitated, collected and sold as a fertilizer byproduct, use of phosphoric acid for black liquor treatment generally remains economically unattractive. The sworn testimony contained in the Rule 132 Declaration from Dr. Harrison R. Cooper expounds on these issues.

Obtaining phosphoric acid from indirect sources, such as phosphate rock, and using the same for treating spent alkaline pulping liquor is the basis of Applicants' invention. First, the various grades of phosphate rock as known in the art are listed herein. 33-39 wt% P_2O_5 is considered high grade phosphate rock, 30-33% is considered intermediate grade, and 26-30% is considered low grade as evidenced by page 17 (attached) in a book by a noted expert in the field of phosphate processing, Pier Becker,

in "Phosphates and Phosphoric Acid: Raw Materials, Technology and Economics of the Wet Processes," 2nd. edition. Marcel Decker Inc., New York, 1989 (hereinafter "Becker"). As described in more detail below, high grade phosphate rock is regarded as too expensive by those having ordinary skill in the art and lower cost low grade phosphate rock is regarded by those having ordinary skill in the art as not being process capable due to a multiplicity of processing problems. Accordingly, it is not surprising that Applicants' use of phosphoric acid obtained from acidulating a phosphate containing material for treating spent alkaline pulping liquor has not been disclosed before the present invention *even though processes for generating phosphoric acid from phosphate rock have been known since before World War I.*

Problems using low grade rock to produce H_3PO_4

Although producing phosphoric acid from phosphate containing rock has been well known for several decades as also evidenced from the cited background in Kopyleva, there are many limiting problems associated with this process, particularly when low grade phosphate rock is used. Pages 6-8 of Becker states that "By its nature, wet process technology conserves most of the impurities found in the original phosphate ore, which are then included in the phosphoric acid produced. Consequently, the variety of the phosphate ores influences not only the process used but also the composition and characteristics of the phosphoric acid produced".

Becker continues "Wet process phosphoric acid technology essentially comprises sulfuric acid attack and separation of the phosphoric acid produced from the calcium sulfate crystals resulting from the reaction. Both the attack and the separation, which is effected by filtration, are considerably affected by the nature of the ore and its

impurities.”..” This separation must be thoroughly completed since, at the price of phosphoric acid, even a small loss at the filter will show up quickly in the economics of the operation.”...

“Without enumerating all the effects on processes and economics due to the impurities, some of the more common are:

1. Effect on crystallization: The calcium sulfate qualities, due to the presence of the various impurities, affect filtration rates by a factor of 4 from one phosphate ore to another.

2. Scaling: Vessels and pipework are subject to deposits of various kinds. Heat transfer coefficients, pressure drop in pipe- work, are subject to heavy alterations.

3. Sludge formation: Some impurities are subject to delayed precipitation in the stored product acid or the final concentrated acid. These are sludges-a difficult problem for the phosphoric acid producer.

4. Corrosion: Despite the use of exotic alloys, pump impellers and agitator turbines can be subject to rapid deterioration by corrosion. “...

The above excerpts from Becker evidences a strong teaching that low grade phosphate rock renders an acidulation process non-manufacturable due to problems with filtration, scaling deposits on piping and vessels, sludge formation and corrosion. Any of these problems can shut the process down. Becker teaches for economical and commercially viable production of phosphoric acid from phosphate rock, high grade phosphate rock (33-39 wt/ %) should be used to produce 27-30% P_2O_5 content in the phosphoric acid solution generated by the process.

Problems using high grade rock to produce H_3PO_4

As noted above, high grade phosphate rock is quite expensive rendering potential application of high grade phosphate rock to spent alkaline pulping liquor processing not economically viable. Without the benefit of hindsight regarding the unexpected valuable products produced by Applicants' process following causticizing, including fertilizer and/or a phosphoric acid source which can be recycled to the acidulator, those having ordinary skill in the art are strongly taught away from use of high grade phosphate rock for spent alkaline pulping liquor processing.

Despite a strong teaching to the contrary, Applicants have unexpectedly discovered that relatively dilute phosphoric acid derived from low grade phosphate rock ($< 30\% P_2O_5$) can be used for the purpose of acidulation of black liquor to precipitate lignin. Importantly, the low grade rock can be used in a single step acidulation process. It was discovered that the dilute phosphoric acid produced from low grade rock without recycling is of low viscosity and the filtration rate is high. Also, it was found that the dilute acid does not lead to the sludge formation and precipitation problems even if impurities are present. Although such a process does not maximize phosphoric acid production as compared to a process where the phosphate material is subjected to acid attack multiple times, a single step process reduces the impurity level in the resulting solution comprising phosphoric acid that is produced, and thus substantially avoids the problems described above by Becker which are based on dissolution of impurities.

Thus, the inventors found that low grade phosphate rock is technically feasible and economically attractive since the cost of this process will be more effective than using phosphoric acid alone. This availability to utilize low grade phosphate rock does

not preclude use of high quality rock if economically available, which can be economically viable based on the revenue derived from the products produced by the claimed method as described above (e.g. fertilizer).

The sworn testimony contained in the Rule 132 Declaration from Dr. Harrison R. Cooper includes compelling evidence of long felt need and the commercial interest already received for the claimed invention. Dr. Cooper provides evidence regarding the failure of numerous past attempts to resolve the requirement solved by the invention, such as at the Rakta Paper Company in Egypt and Central Pulp and Paper Research Institute in India. Dr. Cooper notes that "none [of the previous processes] have met needs of the industry for reasons as being excessively costly in capital and/or operation, or embodied other negative aspects such as producing by-products having little or no marketable value."

Moreover, Dr. Cooper describes a Memorandum of Understanding between the University of Florida and Central Pulp & Research Institute (CPPRI) Saharanpur, India which provides evidence of commercial interest and likely commercial success of the claimed invention. Dr. Cooper notes that the deal is expected to close shortly based on a preliminary financial analysis for typical agro fiber paper mills applying the claimed invention. In view of the above, Applicants submit that claim 1 and its respective dependent claims are patentable over the cited art.

However, certain claims are believed to recite independently patentable limitations. Amended claim 8 which recites a direct causticizing step, the method being exclusive of an intervening evaporating step to remove water from the clarified liquor, wherein a precipitate including at least one calcium phosphate comprising specie is

produced is one such example. Claims 8-10 were rejected under 35 U.S.C. 103(a) as being unpatentable over WO 98/54400 El Shall in view of Kopyleva et al. 5,824,132 as above, and further in view of Kurple 5,034,094. According to the Examiner:

The claims differ from the references as applied above by reciting a step of causticizing the clarified liquor with calcium oxide. Kurple disclose (see col. 2 line 1 through col 4 line 60) that it is known in the art to add calcium oxide to a residual black liquor solution that has been treated with phosphoric acid, to aid in precipitating calcium phosphate from the solution. It would have been obvious to one skilled in the art to modify the references as applied above by utilizing the recited causticizing step in view of the teachings of Kurple, to aid in precipitating calcium phosphate from the black liquor. The specific calcium phosphate precipitated would have been an obvious matter of process optimization to one skilled in the art, depending on the specific black liquor treated and results desired, absent a sufficient knowledge of unexpected results.

Kurple discloses a process where residual solution is evaporated to precipitate sodium sulfate. Crystallized sodium phosphate is dissolved in water then reacted with calcium oxide at high temperature to precipitate calcium phosphate and soluble sodium hydroxide. In his case, Kurple obtains tricalcium phosphate which is of very low solubility as a fertilizer. It is not of economic sense to precipitate calcium phosphate to be sold as fertilizer as taught by Kurple since it is of low solubility and of low price. Thus, it does not justify the use of phosphoric acid to start with.

Claim 8 has been amended to recite the step of *directly* causticizing the clarified liquor after the mixing step using a material comprising calcium oxide, the method being *exclusive of an intervening evaporating step to remove water from the clarified liquor*. Caustic soda and a precipitate including at least one calcium phosphate comprising specie are produced. The method can concentrate sodium phosphate by internal recycle to build strength before adding CaO. Thus, energy of evaporation is saved. The lack of an evaporating step coupled with the resulting caustic soda suitable for recycling and

valuable calcium phosphate products renders the process more economically attractive for small mills which using currently available processes cannot recycle their alkaline pulping reagents.

As noted above, Claim 8 now recites directly causticizing the clarified liquor after the mixing step using a material comprising calcium oxide. Thus, the method recited in amended claim 8 does not precipitate sodium phosphate. Instead, the obtained solution is reacted with CaO directly. Since Kurple evaporates residual solution to precipitate sodium sulfate before the causticizing step, Applicants submit that amended claim 8 is a patentable claim.

Amended claim 9 and 10 recite unique products resulting from Applicants claimed method which are each believed to recite independently patentable limitations. Amended claim 9 recites the calcium phosphate comprising species includes $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Page 12, paragraph 33 of Applicants' specification teaches this product can be formed at a pH of about 4-5. The precipitated calcium phosphate generated under these conditions is of high solubility and can be used as fertilizer. Since Kurple does not disclose or suggest formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, Applicants submit that amended claim 9 recites an independently patentable limitation.

Amended claim 10 recites the calcium phosphate comprising species includes at least one selected from the group consisting of CaHPO_4 , and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Page 12, paragraph 34 of Applicants' specification teaches these product can be formed at a pH of about at least 6. The calcium phosphate precipitated can be recycled for use in the acidulation step. Thus, the needed phosphate rock (as a make up for the phosphate that goes with the gypsum and lignin) will be minimized. This again makes the process cost

effective. Since Kurple does not disclose or suggest formation of any of the recited calcium phosphate products, Applicants submit that amended claim 10 recites an independently patentable limitation.

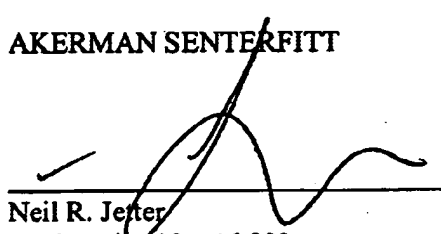
Amended claim 13 recites solid products resulting from the method of claim 8. For reasons described above relating to the differences between products produced following Applicants' direct causticizing step and those produced by Kurple's process. Applicants submit that amended claim 13 is a patentable claim.

Applicants have made every effort to present claims which distinguish over the cited art, and it is believed that all claims are now in condition for allowance. However, Applicants invite the Examiner to call the undersigned if it is believed that a telephonic interview (direct line (561) 671-3662) would expedite the prosecution of the application to an allowance. The Commissioner for Patents is hereby authorized to charge any deficiency in fees due or credit an excess in fees with the filing of the papers submitted herein during prosecution of this application to Deposit Account No. 50-0951.

Respectfully submitted,

AKERMAN SENTERFITT

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Neil R. Jetter
Registration No. 46,803
Akerman Senterfitt
P.O. Box 3188
West Palm Beach, FL 33402-3188
Tel: 561-653-5000

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